

Three-center atomic expansion method for ion-atom collisions

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The three-center atomic expansion method for ion-atom collisions first described by Anderson *et al.* (1974) is reexamined and applied to a broader energy range to study the role of united-atom orbitals in a close collision. In this method the electronic wave function is expanded in terms of traveling atomic orbitals around the two moving centers as well as united-atom orbitals around the center of charge. For the symmetric resonant $H^+ + H(1s)$ collision, it is found that electron-capture probabilities at small impact parameters are changed substantially with the addition of united-atom orbitals at the third center for low-velocity collisions ($v \leq 0.5$), whereas there is almost no such change at higher velocities ($v \sim 1$). This illustrates the velocity range in which the relaxation of electronic orbitals occurs toward the united-atom orbitals in a close collision and implies the velocity range where an adiabatic molecular-orbital expansion becomes inappropriate.

In this report we examine the three-center atomic-expansion method for calculating cross sections for inelastic processes in ion-atom collisions. This method was first described by Anderson *et al.*^{1(a)} and its foundation was discussed by Antal *et al.*² These authors applied the method to calculate charge-transfer and excitation cross sections for $H^+ + H$ by including $1s$ and $2s$ hydrogenic states centered on the two nuclei and the $He^+(1s)$ state of the united atom centered at the *midpoint* of the internuclear line. In our present investigation we retain only the $1s$ orbitals around the three centers in order to assess the importance of united-atom orbitals in the calculation of charge-transfer cross sections. We have developed two different numerical techniques for evaluating three-center matrix elements and applied the

method to calculate electron-capture probabilities. Our total electron transfer cross section at 10 keV differs from the result originally reported by Anderson *et al.*; the difference has been traced to an error in the calculation of the integrated cross section in that paper.^{1(b)} Thus, we demonstrate that the three-center atomic-expansion method does have attractive features deserving further development. We have applied the method to calculate electron transfer cross sections at several other energies and noticed a significant change of capture probabilities $P(b)$ at small impact parameters over those calculated with the two-state two-center model.

In the three-center atomic-state method, the time-dependent electronic wave function $\psi(\vec{r}, t)$ is expanded as

$$\begin{aligned} \psi(\vec{r}, t) = & a_T(t) \phi_T(\vec{r}_T) \exp \left[-i \left[\frac{\vec{v}}{2} \cdot \vec{r} + \frac{1}{8} v^2 t + \epsilon_T t \right] \right] \\ & + a_P(t) \phi_P(\vec{r}_P) \exp \left[-i \left[-\frac{\vec{v}}{2} \cdot \vec{r} + \frac{1}{8} v^2 t + \epsilon_P t \right] \right] + a_C(t) \phi_C(\vec{r}_C) \exp(-i \epsilon_C t) \end{aligned} \quad (1)$$

in a three-state approximation. In the present case of the process $H^+ + H(1s) \rightarrow H(1s) + H^+$, ϕ_T and ϕ_P denote hydrogenic $1s$ wave function (with energy $\epsilon_T = \epsilon_P = -\frac{1}{2}$ a.u.), centered at the target (T) and the projectile (P), respectively. The united-

atom orbital ϕ_C is the $He^+(1s)$ wave function, centered at the center of charge (C), which is also the midpoint of the internuclear line in the present case. The origin of the coordinate system is chosen to be the midpoint of the internuclear line.

The position of the electron is denoted by \vec{r} with respect to the origin of the coordinate system, and by \vec{r}_i ($i=T,P,C$) with respect to the other centers. Notice in the present case that there is no electron translational factor associated with the third center because it coincides with the chosen origin of the coordinate system.

Substituting Eq. (1) into the time-dependent Schrödinger equation and following the standard close-coupling method, a set of first-order coupled equations for $a_T(t)$, $a_P(t)$, and $a_C(t)$ are obtained with the initial conditions $a_T(-\infty)=1$, $a_P(-\infty)=a_C(-\infty)=0$, and the equations are integrated to obtain $a_i(+\infty)$ ($i=T,P,C$) for each impact energy E and impact parameter b . The transition amplitudes $a_T(+\infty)$ and $a_P(+\infty)$ are easily identified as the elastic and charge-transfer amplitudes, respectively. The amplitude $a_C(+\infty)$ can be interpreted as an estimate of the ionization amplitude as has been discussed by Anderson *et al.*¹ In our calculation, straight-line trajectories are assumed.

The coefficients of the coupled equations in this model include some one- and two-center matrix elements which are calculated in a standard way.³ The three-center matrix elements with electron translational factors of the form

$$\langle \phi_A | V_B \exp(i\vec{v}\cdot\vec{r}_C) | \phi_C \rangle$$

are calculated by two different methods: (1) by defining elliptical spheroidal coordinate (λ, μ, ϕ) with respect to the two center P and T , the matrix can be reduced to a two-dimensional numerical integration over λ and μ (the ϕ integration being analytical); (2) by expressing the wave functions in terms of Gaussian orbitals, the integral can be reduced to a one-dimensional numerical integration over λ . In a test at $E=120$ keV and $b=0.2, 4.0$, probabilities calculated with matrix elements from these two methods differ by at most 0.0005. It is to be noted that these two methods are different from the one used by Anderson and Antal.⁴ These authors evaluated the three-center integrals using a method similar to that used by Cheshire⁵ where the two-center integrals were evaluated by solving a set of coupled linear first-order equations.

Using the three-state three-center atomic-expansion model described above, we have calculated the charge-transfer probabilities $P(b)$ for 2 keV $\leq E \leq 25$ keV in $H^+ + H(1s) \rightarrow H(1s) + H^+$ collisions, as well as integrated cross sections. The tighter united-atom orbitals included will allow the system to relax for close collisions at small velocities in a similar way as molecular orbitals do. On

the other hand, such relaxation is not expected to be important for collisions at large impact parameters or at higher collision velocities. Thus, we shall expect the inclusion of united-atom orbitals to have an effect on electron transfer probabilities $P(b)$ only for small impact parameters ($b \leq 1$ a.u.) and the effect will become less important with increasing velocities, as far as allowing for the relaxation of the basis orbitals is concerned. Since the integrated total electron transfer cross sections for symmetric collisions are dominated by capture at large impact parameters, the integrated cross section in the present three-center three-state calculation is not expected to differ very much from the corresponding two-center two-state result.

In Figs. 1(a)–1(d) we display the electron transfer probabilities versus impact parameter for $E=2, 5, 10$, and 25 keV calculated according to three different theoretical models. The dashed lines give the results of the simple two-state two-center atomic-expansion method in which only the orbitals around the target and the projectile center are retained. The results of the present three-state three-center calculations are shown as solid lines. (The two-center four-state calculations, to be described in the next paragraph, are shown as crosses.) We notice that the three-center three-state results do differ significantly from the two-center two-state results at small impact parameters $b \leq 1$ a.u. At larger impact parameters the difference is very small and can be practically neglected. At $E=25$ keV, the difference is fairly small even at small impact parameters, indicating that the dynamical system does not develop through transitionally formed united-atom orbitals at this and higher energies even for close collisions. It should be pointed out that amplitudes $a_C(+\infty)$ in all of these cases are very small; the substantial change of capture amplitude due to the introduction of the third center is thus more directly due to the inadequacy of the two-center two-state basis set for describing the relaxation of the electronic orbitals at close collisions rather than to the neglect of coupling with ionization channels.

In Fig. 1(a)–1(d) we also show the results of two-center four-state calculations⁶ in which $H(1s)$ and $He^+(1s)$ wave functions centered on the nuclei are included. The $He^+(1s)$ orbital used at each center in this calculation has been orthogonalized to the $H(1s)$ wave function on that center and has an energy expectation value in the continuum. The pseudostate thus introduced does have the tight-orbital component of $He^+(1s)$, which might repro-

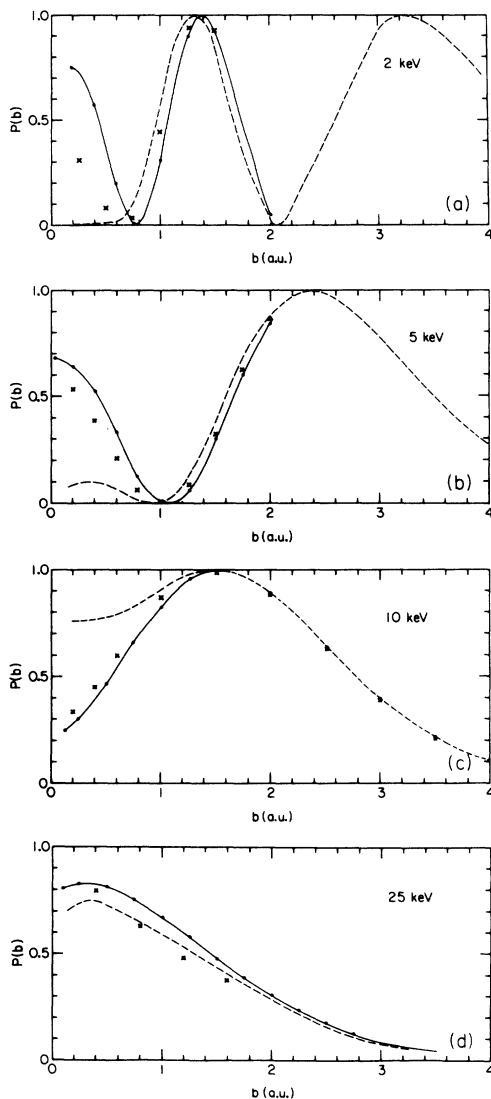


FIG. 1. Charge-transfer probabilities $P(b)$ vs impact parameter b for the collision $H^+ + H(1s) \rightarrow H(1s) + H^+$ at laboratory-collision energies 2, 5, 10, and 25 keV. The dashed lines are from the two-state two-center atomic-expansion calculation. The solid lines give the results of the three-center atomic-expansion calculation, with dots indicating the actual calculated points. The crosses are from the four-state two-center calculations.

duce some of the features of the three-center expansion model. However, it is to be noticed that these united-atom orbitals are not centered at the center of charge and that they, therefore, are attributed plane-wave translation factors in the same way as the separated-atom orbitals are. The degree of agreements between the two-center four-state model results and the three-center results shown in

Fig. 1(a)–1(d) indicates that the positioning of the united-atom orbitals does have some effect on the calculated capture probabilities.

At energies shown in Fig. 1(a)–1(d), the integrated electron-capture cross sections agree closely (within 3%) in all three theoretical models discussed above since integrated total-capture cross sections are dominated by contributions from larger impact parameters. The present integrated-capture cross section at 10 keV from the three-state three-center model is 7.8 \AA^2 which agrees fairly closely with the corrected five-state three-center value 7.5 \AA^2 of Anderson *et al.*^{1(b)} At 2, 5, and 25 keV, three-state three-center cross sections have been calculated to be 13.7, 9.90, and 3.03 \AA^2 ; the corresponding two-state two-center values are 13.5, 9.90, and 2.76 \AA^2 . These results agree quite well with experimental values and with calculations including pseudostates.⁷

The results shown in Fig. 1(a)–1(d) indicate that measurements of integrated total-capture cross sections will not provide a critical test of the theoretical models for charge transfer at energies considered in this article. A direct test will be to compare with experimental data at small impact parameters.

The only experimental data of this nature are

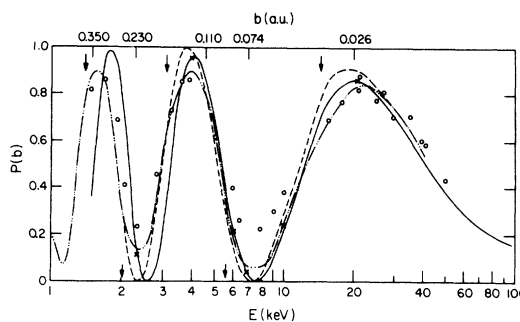


FIG. 2. Total charge-transfer probability $P(b)$ vs collision energies for $H^+ + H(1s) \rightarrow H(1s) + H^+$ at the fixed scattering angle of 3° . Experimental data, shown as open circles, are taken from Helbig and Everhart (Ref. 8). Theoretical results; \cdots two-center atomic plus pseudostate including $1s$, $2s$, $2p$, $3\bar{s}$, $3\bar{p}$ states (Cheshire *et al.*, Ref. 7). --- , present three-center three-state results [earlier results of Anderson *et al.* (Ref. 1) are shown as crosses]; --- present two-center $1s$ and $1\bar{s}$ atomic-state results where $1\bar{s}$ is the $He^+(1s)$ wave function orthonormalized to the $H(1s)$ wave function. The predicted positions of maxima and minima of the oscillation in the two-state two-center results are indicated by arrows.

the so-called 3° oscillations of $P(b)$ measured by Helbig and Everhart (1964).⁸ By measuring the electron-capture probabilities at 3° scattering angle at varying scattering energies, they observed that $P(b)$ shows oscillatory variation with scattering energies. In Fig. 2 their data are shown together with results from theoretical models. The arrows indicate the predicted collision energies where maxima and minima of $P(b)$ occur according to the two-state model. The solid line is the three-center result and the dash-dotted lines are from the pseudostate (seven states on each center) calculations of Cheshire *et al.*⁷ The results from Anderson *et al.*^{1(a)} (denoted by circles) are identical to our present three-center results. The two-center four-state results are indicated by dashed lines. We notice that the latter three models all predict the positions of maxima and minima in good agreement with the experimental data. In Fig. 2 we show on the top scale the impact parameters corresponding to 3° at the collisions energies shown on the bottom scale. [There is little dependence of $P(b)$ on b and scattering angles at these small impact parameters. The values shown can be viewed as the approxi-

mate probabilities at zero-impact parameter.] We notice that only very small impact parameters are tested in these studies.

In summary we show that the incorporation of united-atom orbitals in a three-center atomic-expression method does allow the electronic system to relax toward molecular orbitals for close collisions at low velocities. In a sense, unlike the molecular-orbital (MO) expansion in a small basis set, the relaxation is not "forced" into the collision system by choosing fully relaxed molecular orbitals in the expansion; rather, the collision system actually chooses dynamically to relax if the conditions are favorable and not to relax if the conditions are not favorable. Our results indicate this method should be explored further with additional states on each of the three centers. The inclusion of states is to be guided by molecular-correlation diagrams.

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